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Antimony dispersion at abandoned mines in Sardinia, Italy

Rosa Cidu*, Riccardo Biddau, Elisabetta Dore, Andrea Vacca

University of Cagliari, Dipartimento di Scienze Chimiche e Geologiche, via Trentino 51, 09127 Cagliari, Italy

Abstract

Aqueous Sb may result from both natural and human processes. The World Health Organization has established a guideline value of 20 µg/L Sb for drinking water. Concentrations of Sb above drinking water standards may occur in water draining abandoned mines. The Sb occurrence in water and potential dispersion in the atmosphere were investigated at Su Suergiu (Sardinia, Italy). The Su Suergiu Sb ores were exploited between 1880 and 1980, with mining and processing residues abandoned on site. Surface waters downstream of the mine show high concentrations of Sb (up to 1500 µg/L). Contamination extends several km downstream of the mine and affects the Flumendosa River, water from which is used for irrigation and domestic purposes. Dust materials deposited on leaves collected in the mine area contain 70 µg/kg Sb, as compared to 7 µg/kg Sb observed on leaves collected on upstream slopes.

Keywords: aqueous antimony; antimony dispersion; mine water; abandoned mine; Sardinia

1. Introduction and study area

Antimony is categorized as a non-essential element for plants, animals and humans, while it is listed as a priority pollutant by the US Environmental Protection Agency and the World Health Organization. The mobility, bioavailability and toxicity of Sb depend on its speciation. Aqueous Sb may occur as antimonous and antimonic acids with related species, respectively under reducing and oxidizing conditions. However, thermodynamically unstable Sb species may occur under different redox conditions, suggesting that the kinetics of redox reactions may play a significant role in defining the impact and fate of Sb in the environment [1]. Atmospheric Sb compounds may derive from waste incineration, fossil fuel combustion, ore smelting, and road traffic [2], with Sb in airborne matter estimated at ng/m^3 level, and higher values in urban areas [3].

This study aims to investigate the occurrence and speciation of Sb in waters impacted by past Sb mining and to evaluate the Sb dispersion in the atmosphere. The study area is located at Su Suergiu (SE

* Corresponding author. Tel.: +39-070-6757724; fax: +39-070-282236.
E-mail address: cidur@unica.it.

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Sardinia, Italy). The Sb-W deposits hosted in Paleozoic black schists and limestone were exploited since 1880 until mine closure in 1960. A foundry was active from 1882 to 1987. The most abundant minerals are antimonite, scheelite, arsenopyrite, pyrite, with calcite and quartz in the gangue. Slag and tailings (87% of dumped materials) and waste rocks were dumped nearby the mine plant (Fig. 1). Mining and processing residues are estimated at about 66,000 m^3 [4]. Leptosols are the main soils in the area, and Cambisols occur on slopes and colluvial deposits. Mean annual precipitation is 670 mm, and temperature 16 °C. Springs usually have flow <0.1 L/s. The flow of streams varies depending on rainfall. Untreated drainage from Su Suergiu flows into the Rio Ciurixeda stream, a tributary of the Flumendosa River that supplies water for agricultural and domestic uses.

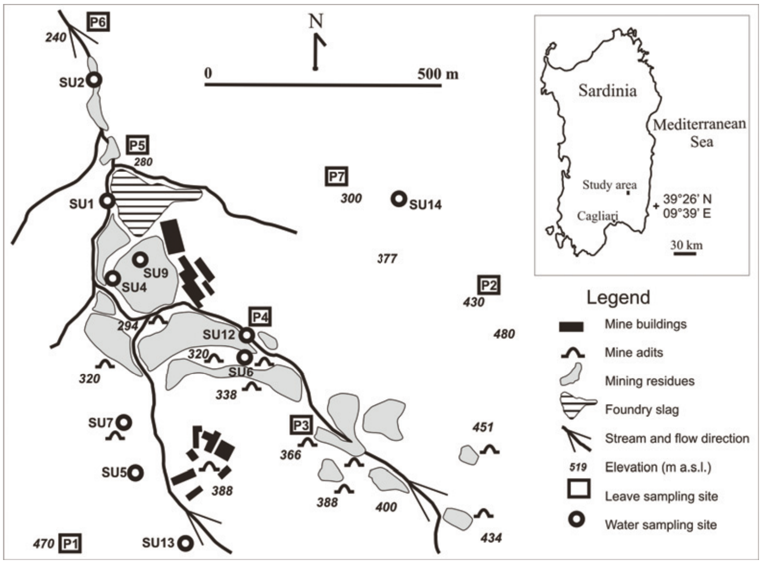

Fig. 1. Map showing the Su Suergiu mine area and location of sampling sites

2. Methods

Water and vegetation samples were collected in spring 2012. Water samples consist of springs, mine drainage, and water draining slag materials (Fig. 1). The physical–chemical parameters and alkalinity were measured on site; water was filtered (0.45 µm) and acidified to 1% HNO_3 for metal analysis and total Sb by quadrupole ICP–MS using Rh as internal standard. A filtered aliquot was acidified to 1% HNO_3 and 0.2% (L+) tartaric acid for Sb(III) analysis by adsorptive stripping voltametry (Metrohm 797 VA Computrace, hanging Hg drop electrode in 0.6 M HCl). Sb(V) was calculated subtracting Sb(III) from total Sb. To evaluate the potential Sb dispersion in the atmosphere, 23 leaf samples (*Pistacia lentiscus*) were collected (Fig. 1) in PE bags and stored at 4 °C. In the lab, 25 g of leaves were washed with 250 mL of 0.01 M HCl, used as a proxy of rainwater, and shaken for few minutes. The solution was filtered at 0.4 µm, reduced to 50 mL final volume, acidified with HNO_3 and analyzed by ICP-MS.

Results

Table 1 reports values of flow, pH, redox potential (Eh), electrical conductivity (EC), dominant composition, and concentrations of sulfate and antimony in the studied waters. It is worth mentioning that results of hydrogeochemical surveys carried out in 2012 are similar to those observed in previous studies carried out in 2005 and 2006 [5]. Local spring waters collected upstream of the mine area show slightly alkaline pH, relatively low conductivity and sulfate (Table 1). In these waters, Sb concentrations are below the WHO guideline value for drinking water (i.e. 20 μg/L Sb) [6], and are similar to mean values observed in Sardinian rivers [7]. Background concentrations of antimony in groundwater of Sardinia from metamorphic rocks are estimated between 0.1 and 1.3 μg/L [8].

Table 1. Physical-chemical parameters, dominant ionic composition, concentrations of sulfate and antimony in the studied waters.

Sample	Type	Flow	pH	Eh	EC	Dominant ions	SO_4^{2-}	Sb tot	Sb(III)
		L/s		V	mS/cm		mg/L	μg/L	μg/L
SU5	S	nd	7.4	0.46	0.31	HCO_3 - Ca (Na)	39	4.2	<0.3
SU13	S	nd	7.0	0.49	0.36	HCO_3 - Ca (Na)	49	1.4	<0.3
SU9	B	nd	7.0	0.44	2.18	SO_4 - Ca	1200	99	1.1
SU4	A	0.1	7.1	0.37	0.79	HCO_3 (SO_4) - Ca	180	490	0.7
SU6	A	0.05	7.8	0.46	0.90	SO_4 - Ca	310	850	1.3
SU7	A	0.01	7.8	0.47	0.46	SO_4 (HCO_3) - Ca (Na)	120	225	0.4
SU12	A	0.01	8.1	0.46	2.64	SO_4 - Ca	1600	890	0.9
SU1	D	0.05	7.7	0.35	1.50	SO_4 - Ca	670	4700	20
SU2	D	0.05	8.4	0.42	1.79	SO_4 - Ca	820	15000	120

S: spring; B: borehole; A: adit drainage; D: slag drainage

In mine drainages located upstream of the slag heap conductivity increases, especially due to the increase in sulfate and calcium, and concentrations of Sb (up to 850 μg/L) are much higher than local groundwater (Table 1). Water samples interacting with slag materials are characterized by extreme concentrations of Sb (up to 15 mg/L), clearly indicating that these materials are the main source of contamination at Su Suergiu. Drainages from the slag heap and adits flow into the Rio Ciurixeda. Despite the fact that flow of contaminated waters is usually low (<1 L/s), the Rio Ciurixeda shows elevated concentrations of Sb (i.e. 1300 μg/L Sb) [9]. The Sb contamination extends to the Flumendosa River, several km downstream of the Rio Ciurixeda confluence.

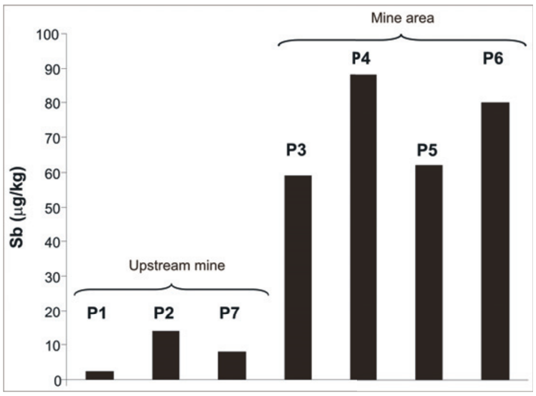

Fig. 2. Concentrations of Sb leached from leaf samples.

Fig. 3. View of the slag heap at Su Suergiu.

Speciation results show that Sb(V) is the predominant form, while Sb(III) is a minor constituent in waters at Su Suergiu. The highest concentration of Sb(III), i.e. 120 μg/l, was observed in water draining the slag materials, and corresponded to about 1% of total antimony. Slightly alkaline pH and oxidizing conditions in the Su Suergiu waters might favor the stability of Sb(V) in solution, while the Sb(III) species might be preferentially removed due to their high affinity to particulate phases [10].

The Sb-bearing fine particles carried by the wind in the atmosphere can be deposited on vegetation, then fall again to the ground. Fig. 2 shows mean concentrations of Sb leached from the leaf samples collected in the mine area (Fig. 1). Dust materials deposited on vegetation samples collected on the slopes upstream of the mine area contain a mean of 7 μg/kg Sb, while concentrations of Sb deposited on leaves collected in the mine area are much higher, with a mean of 70 μg/kg Sb.

3. Conclusions

Results of this study demonstrate that the major process controlling antimony contamination at Su Suergiu is the Sb release from the abandoned slag materials (Fig. 3). Drainage from the slag heap affects the Flumendosa river several km downstream of the mine area. Therefore, remediation actions should be addressed to avoid the contact of water with the slag materials and to reduce erosion of the slag heap.

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